

## Vinyl lactam copolymers as gas hydrate inhibitors

## Description

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The invention relates to the use of copolymers composed of from 40 to 99.5% by weight of at least one ethylenically unsaturated lactam A

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from 0.5 to 60% by weight of monomers B having a water solubility of less than 10 parts by weight of monomer in 100 parts by weight of water and

15 from 0 to 50% by weight of other monomers C

as gas hydrate inhibitors.

It is known that gas hydrates, also known as clathrate hydrates, can form under certain conditions in media which comprise gas molecules such as CO<sub>2</sub> or hydrocarbons, e.g. C<sub>1</sub>-C<sub>4</sub>-alkanes, and water. These gas hydrates consist of the gas molecules mentioned which are surrounded by a "cage" of water molecules. Such gas hydrates also occur in water-containing mineral oil or natural gas mixtures and can thus lead to blockage of the pipelines, for example, in the course of transport.

In order to prevent this, gas hydrate inhibitors are added to the mineral oil or natural gas mixtures.

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WO 94/12 761, WO 95/32 356 and DE 19935063 disclose polymeric additives for the prevention of clathrate hydrates in liquid systems which have a comonomer having a lactam ring in the polymer.

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DE-A-10010811 discloses the use of homo- and copolymers in solvents having a high flashpoint as gas hydrate inhibitors. EP-A-795567 discloses copolymers of vinyl lactams having hydrophobic monomers.

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There is a need for improved gas hydrate inhibitors which are simultaneously very easy to prepare and thus inexpensive.

In particular, the gas hydrate inhibitors should prevent the formation of gas hydrates even at very low temperatures.

It is an object of the present invention to provide suitable polymers for use as a gas hydrate inhibitor, which satisfy the requirements to a very high degree.

5 Accordingly, the use defined at the outset has been found.

Monomers A are present in the copolymer preferably to an extent of at least 60% by weight, more preferably to an extent of at least 70% by weight; their proportion is preferably a maximum of  
10 up to 99% by weight, more preferably up to 95% by weight.

The proportion of monomers B is preferably at least 5% by weight, more preferably at least 10% by weight, but preferably does not exceed 40% by weight, in particular 30% by weight.

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It is not necessary to also use monomers C in the context of the invention; the proportion of monomers C is therefore, for example, below 20% by weight, below 10% by weight and in particular 0% by weight.

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The copolymer used as a gas hydrate inhibitor is, for example, preferably composed overall of

from 60 to 99% by weight of A,  
25 from 1 to 40% by weight of B and  
from 0 to 39% by weight of C.

It is more preferably composed of

30 from 70 to 90% by weight of A,  
from 10 to 30% by weight of B and  
from 0 to 20% by weight of C

and most preferably of

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from 78 to 88% by weight of A and  
from 12 to 22% by weight of B.

The monomers A are cyclic or noncyclic lactams, or vinyl lactams.

40 Noncyclic vinyl lactams include N-vinyl amides, in particular  
N-vinyl-N-methylacetamide.

Monomers A are preferably cyclic lactams, in particular  
N-vinylcaprolactam or N-vinylpyrrolidone or mixtures thereof.

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They are more preferably N-vinylpyrrolidone.

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Monomers B are monomers, other than monomers A, having a solubility in water of less than 10 parts by weight, preferably less than 5 parts by weight, more preferably less than 1 part by weight, most preferably of less than 0.1 part by weight and in particular of less than 0.05 part by weight in 100 parts by weight of water at 21°C.

Monomers having corresponding solubility are in particular selected from C<sub>1</sub>- to C<sub>20</sub>-alkyl (meth)acrylates,  
10 C<sub>1</sub>-C<sub>20</sub>-alkyl(meth)acrylamides, e.g. t-butylacrylamide, vinyl esters of carboxylic acids containing up to 20 carbon atoms, styrenics having up to 20 carbon atoms, ethylenically unsaturated nitriles, vinyl halides, vinyl ethers of alcohols containing from 1 to 10 carbon atoms, aliphatic hydrocarbons having from 2 to 8  
15 carbon atoms and one or two double bonds, or mixtures of these monomers.

The monomers are more preferably selected from: C<sub>1</sub>-C<sub>20</sub>-alkyl (meth)acrylates or vinyl esters of carboxylic acids having up to  
20 20 carbon atoms.

They are even more preferably C<sub>1</sub>- to C<sub>8</sub>-alkyl acrylates or C<sub>1</sub>- to C<sub>8</sub>-alkyl methacrylates, in particular C<sub>2</sub>-C<sub>8</sub>-alkyl (meth)acrylates and more preferably C<sub>4</sub>-C<sub>8</sub>-alkyl (meth)acrylates, in particular  
25 n-butyl acrylate or 2-ethylhexyl acrylate.

Useful monomers C other than monomers A and B are any other monomers, for example also monomers having functional groups, for example carboxylic acid, hydroxyl or amino groups. Examples  
30 include hydroxy (meth)acrylates, (meth)acrylamide, (meth)acrylonitrile or (meth)acrylic acid or acrylamidomethylpropanesulfonic acid or salts thereof.

Preference is given to using the copolymers in the form of the  
35 solution or dispersion thereof.

Useful solvents include water, polar organic solvents such as alcohols, carboxylic esters or nonpolar solvents such as aliphatic or aromatic hydrocarbons.

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Preference is given to solvents having a flashpoint greater than 50°C, more preferably greater than 61°C and most preferably greater than 100°C.

45 The flashpoint is determined to DIN EN 22719.

Solvents having a flashpoint greater than 61°C or greater than 100°C are, for example, 1,2-ethanediol (111°C) and 1,2-propanediol (107°C).

- 5 The K value of the copolymer is preferably from 10 to 100, more preferably from 10 to 45 and even more preferably from 15 to 40 and in particular from 22 to 37 (measured on a solution having 5 parts by weight of copolymer to 100 parts by weight of ethanol at 21°C).

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The copolymer can be prepared by customary methods of free-radical polymerization.

Examples include emulsion polymerization or solution  
15 polymerization.

- The polymerization may be carried out in the presence of customary free-radical initiators such as peroxides or azo compounds (amount, for example, from 0.1 to 10% by weight based  
20 on the monomers) in a solvent, if appropriate under pressure, at temperatures between 50 and 160°C. The presence of substances which regulate the polymerization may also be advantageous. The monomers may preferably be fed in a feed process during the polymerization. In the case of very greatly differing  
25 reactivities of the monomers, possible methods also include a staged method, gradient method or feed rate controlled separately for each monomer.

- The solids contents of the resulting solutions or dispersions are  
30 generally from 10 to 65% by weight, preferably from 25 to 45% by weight.

- In a particular embodiment, the copolymer is prepared directly in a solvent having a high flashpoint, so that the abovementioned,  
35 preferably used solutions are obtained immediately in the course of preparation.

- In such a preparation process, it may be necessary to dissolve and use individual additives, for example the initiator, in  
40 another solvent having a lower flashpoint than desired.

Such solvents may be removed later, for example by distillation.

- A corresponding process is described, for example, in  
45 DE 10010811.

The copolymers or the solutions or dispersions thereof are used as gas hydrate inhibitors.

It is possible for this use to add further additives to the solutions or dispersions.

Examples include further solvents, corrosion inhibitors, viscosity regulators, stabilizers, other gas hydrate inhibitors, assistants for preventing agglomerations, for example antiagglomerates.

The copolymers or the solutions or dispersions thereof are especially suitable for mineral oil or natural gas; they are notable for high effectiveness as a gas hydrate inhibitor even at low temperatures and at small amounts used.

#### Examples

##### Polymers used

- polyvinylpyrrolidone, dissolved in water, solids content 30% by weight
- polyvinylcaprolactam, dissolved in ethylene glycol, solids content 40% by weight
- copolymer of 80% by weight of vinylpyrrolidone, 20% by weight of n-butyl acrylate, 40% by weight solution in ethylene glycol

##### Preparation of the copolymer:

			Conc.	phm
Initial charge	1080.00 g	of ethylene glycol	100.00%	54.82
	200.00 g	of isopropanol	100.00%	10.15
	40.00 g	of vinylpyrrolidone	100.00%	2.03
	120.00 g	of feed 1		
Feed 01	800.00 g	of ethylene glycol	100.00%	40.61
	1530.00 g	of vinylpyrrolidone	100.00%	77.66
	400.00 g	of n-butyl acrylate	100.00%	20.30
Feed 02	200.00 g	of isopropanol	100.00%	10.15
	40.00 g	of tert-butyl peroxy-ethylhexanoate	98.00%	1.99
	200.00 g	of ethylene glycol	100.00%	10.15

The initial charge is heated to internal temperature 85°C. 5 g of feed 2 are then added at 80°C and the mixture is polymerized for 3 - 5 minutes. Afterward, feed 1 within 5 hours and feed 2 within 6.5 hours are metered in. On completion of the addition of feed 5 2, polymerization is continued for another 3 hours. Volatile fractions are removed by vacuum distillation. Solids content 49.2% by weight.

The K values of the polymers are reported in the table; they are 10 determined on a 5% by weight polymer solution in ethanol.

Use as a gas hydrate inhibitor

The suitability of the polymers as a gas hydrate inhibitor is 15 determined from the initial freezing temperature of mixtures which comprise the polymers.

The "initial freezing temperature" was measured by the "ball-stop method" analogously to the test method described in Example 1 of 20 WO 95/32356.

This method relates to initial freezing points to be tested of water/THF mixtures by addition of different polymers (proof of hydrate formation) which have been frozen in a 0.5% concentration 25 in a water/THF (81/19% by weight) mixture.

To determine the initial freezing point of various polymer/(water/THF) mixtures, the following equipment and reagents are needed:

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- water/THF mixture (81/19% by weight)
- thermostat bath with water/ethylene glycol (5/1) refrigerant mixture
- constant stirrer
- 35 - holder for test tubes (5 ml)
- small stainless steel balls for better mixing in the test tube

A 0.5% solution of the polymer to be investigated is prepared in 40 water/THF (81/19). The test tube is 2/3 filled, provided with a small stainless steel ball, sealed and secured in the test tube holder. The measurement is started at bath temperature 4°C and a rotation rate of 20 rpm and the temperature is reduced by 0.5°C per hour until the sample has started to freeze, i.e. the steel 45 balls no longer move in the test tube. A blank sample runs in parallel to each measurement.

The initial freezing temperature is specified in the table which follows. The lower the initial freezing temperature, the better the suitability as a gas hydrate inhibitor generally is.

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	Polymer	K value	Initial freezing temperature °C
	None	-	4.0
	Polyvinylpyrrolidone	30	2.5
10	Polyvinylcaprolactam	26	0.5
	Inventive polymer (80 VP 20 nBA)	30.6	-1

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